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REVIEW OF RECENT DEVELOPMENTS

Refractory Metals (Cb, Ta, Mo, W)

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GENERAL

The Refractory Metals Sheet Rolling Panel has officially concluded its formal program covering a 6-year period. A summary report covering the objectives, activities, and achievements of this program has been made available.(1)

COLUMBIUM AND TANTALUM TUBING

The corrosion behavior of potential columbium and tantalum tubing alloys for advanced turboelectric space-power systems was evaluated by NASA(2) by refluxing potassium (20 ppm O_2 max) at 1800 to 2400 F for time periods up to 4000 hours at 10^{-7} to 10^{-8} torr. The alloys could be grouped in order of decreasing resistance to corrosion by refluxing potassium as follows:

Good Resistance	Marginal Resistance	Unsatisfactory Resistance
T-111	Cb-1Zr	B-33
T-222		SCb-291
C-129		Ta-10W
D-14		
Cb-752		
D-43		
AS-55		
B-66		
FS-85		

It was found that the gettered refractory-metal alloys, i.e., those containing reactive elements zirconium and hafnium, are more resistant to corrosion by refluxing potassium than are the ungettered alloys.

Phase III of a four-phase program to develop the manufacturing techniques for the production of high-strength tantalum alloy tubing at Allegheny Ludlum is near completion.(3) Both Ta-10W and T-222 can be subjected to the same processing schedules with comparable results in the finished tubing. Both alloys exhibited excellent drawability with area reductions of up to 62 percent without intermediate annealing. Elevated-temperature tensile and creep-rupture tests are in progress.

COLUMBIUM

Fansteel has reported final results on the second study under Navy sponsorship on the fabrication of production heats of FS-85 columbium-base alloy.(4) The present study involved larger ingots (9-inch diameter) and extrusion directly to sheet bar rather than side forging to sheet bar. Material properties were found to be uniform from heat to heat and consistent with current production heats. Recrystallization behavior and tensile properties of FS-85 are summarized in Tables 1 and 2, respectively.

The creep-rupture properties of FS-85 alloy has been determined up to and exceeding 1000 hours at temperatures to 2600 F at Oak Ridge.(5) Rupture curves are shown in Figure 1. Substantial improvements in strength at 1800 and 2200 F were achieved by pretest annealing recrystallized material which had been annealed for 1 hour at 2500 F for an additional 1 hour at 2900 F. Improvements were stable for at least 1000 hours. Pretest annealing at higher temperatures yielded inferior time-dependent properties.

Westinghouse has determined the solid-solubility limits of oxygen, nitrogen, and carbon in the columbium-molybdenum system.(6) At oxygen pressures above 10^{-14} torr, columbium is in equilibrium with oxide vapor and takes in 4.7 at.% at 2730 F. This decreases with increasing molybdenum content to 1.7 at.% in an alloy containing 10 at.% molybdenum. The addition of molybdenum to columbium drastically reduces the amount of nitrogen that can be retained in solid solution. At 3990 F, the maximum nitrogen content drops from about 14.5 at.% for unalloyed columbium to almost zero at 10 at.% molybdenum. Less than 0.5 at.% carbon can be retained by pure columbium at 3630 F, and is little changed with molybdenum content. With carbon contents greater than 0.5 at.% and molybdenum contents up to 48 at.%, the phase in equilibrium with the columbium-molybdenum primary solid solution was identified as Cb_2C.

TANTALUM

A long-range program is under way at McDonnell under Air Force sponsorship for the development of a self-sustaining, radiating, coated-tantalum structure for extended high-temperature service.(7) A study of conceptual vehicles and trajectories has produced two trajectories and associated configuration characteristics that will develop a peak temperature of 3600 F on a leading-edge component and a flat-panel component. The program is divided into three phases starting with surveys on tantalum alloys, coatings, and insulating materials and property tests of promising coated tantalum "materials systems". The program is to continue in later phases with fabrication assessment of the best systems and procedures and with the design, fabrication, and testing of full-scale components.

TABLE 1. RECRYSTALLIZATION BEHAVIOR OF FS-85 ALLOY(4)

1-Hour Annealing Temperature, F	Hardness, DPH	Structure
As rolled (50 percent)	275	No recrystallization
2010	220	No recrystallization
2100	220	No recrystallization
2190	215	50 percent recrystallization
2280	200	70 percent recrystallization
2370	190	100 percent recrystallization - ASTM 8
2460	193	ASTM 8
2550	195	ASTM 6

TABLE 2. TENSILE PROPERTIES OF FS-85 ALLOY(4)

Heat	Direction	Condition	Tensile Strength, 1000 psi	Yield Strength, 1000 psi	Elongation, percent	Elastic Modulus, 10^6 psi
		Room Temperature				
1	L	Stress relieved	96.7	83.8	16	[illegible]
	T		104.4	91.3	13	20.[illegible]
2	L	Stress relieved	100.7	87.5	16	20.0
	T		109.9	97.9	11	20.4
1	L	Recrystallized	84.9	68.5	23	20.1
	T	Recrystallized	88.2	73.1	23	20.6
2	L	Recrystallized	86.7	69.3	23	20.8
	T	Recrystallized	90.8	75.6	21	20.6
		2000 F				
1	T	Stress relieved	51.4	48.7	20	12.9
	T	Recrystallized	38.0	28.2	33	12.7
2	T	Stress relieved	57.4	55.2	17	--
	T	Recrystallized	40.8	31.3	27	--

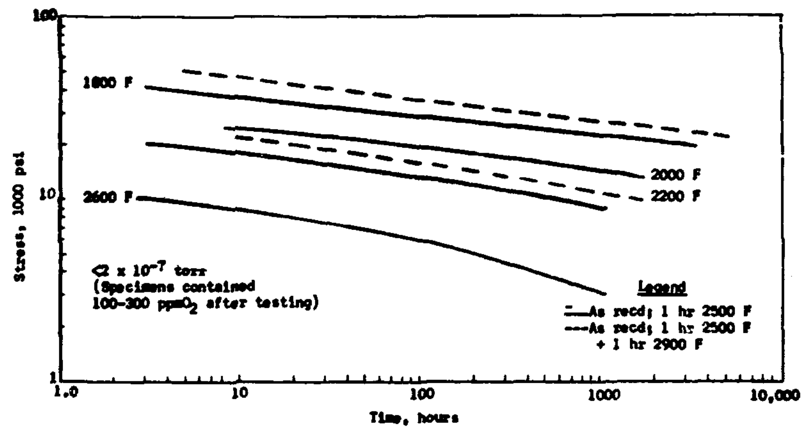

FIGURE 1. STRESS-RUPTURE PROPERTIES OF FS-85 ALLOY(5)

To date, three alloys, Ta-9.6W-2.4Hf-0.01C (T-222), Ta-7W-3Re (Type 473), and Ta-10W-2.5Mo, have been selected from a list of nine candidate alloys as having the best combinations of desired properties. At the present time, only the tungsten barrier-silicide coating concept appears promising for the protection of structural-tantalum sheet-metal airframe components for the life requirement of 1 hour at 3600 F.

Additional long-time, high-vacuum creep data for T-111 alloy have been reported by TRW and are summarized in Figure 2.(8) Future efforts will be directed toward the determination of Manson-Haferd constants for T-111 material.

Westinghouse has successfully converted a 4-inch-diameter ingot of Ta-8W-1Re-0.7Hf-0.025C to sheet in a property evaluation of the potential use of the alloy in advanced space-power systems.(9) The evaluation of weldability, creep resistance, and fabricability characteristics of this alloy are in progress. Two other optimized alloy compositions are to be selected for similar scale-up and evaluation.

MOLYBDENUM

Allegheny Ludlum Steel has reported the su cessful fabrication of H-shaped extrusions of mo denum TZM alloy.(10) Extrusions 15 feet long we fabricated having 0.070-inch and 0.080-inch web thicknesses. Both sizes required severe extrusi conditions of 3300 F billet temperature and [illegible] pressures up to 230,000 psi. Improvement in die performance was obtained by the use of a 0.050-i thick zirconia coating on the die applied by the plasma-spraying process.

Attempts to warm draw these extrusions us a standard production-type draw bench were gene unsuccessful. Results of drawing trials reveal that the H-shaped sections were very sensitive temperature and processing loads.

Ipson Industries has reported the results a program to explore the production of foamed metals.(11) Foamed molybdenum was produced by suspending molybdenum powders in a liquid conta binders, cements, and foaming agents. This slu was foamed by entraining air under conditions th caused bubbles of gas to be distributed through

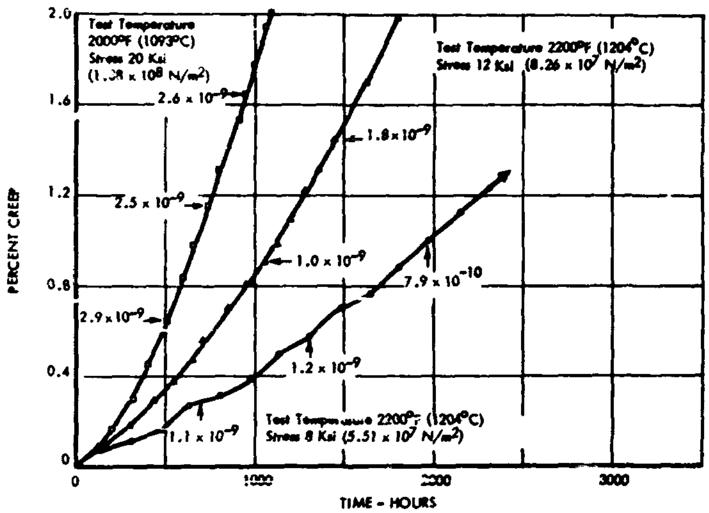

FIGURE 2. CREEP DATA FOR ANNEALED (1 HOUR AT 3000 F) T-111 AT 2000 AND 2200 F (8)

the suspension. The suspension is subsequently dried to set the cements and binders. The dried slabs are then vacuum sintered to volatilize the binders, cements, and foaming agent, leaving essentially a slab of bonded metal particles. Slabs ranging from 12 to 30 percent of theoretical density were produced.

The foamed metal was found to have many of the original characteristics of solid molybdenum and could be cut and machined by normal shop techniques. However, because the metal was very porous, the tensile, compressive, and flexural strengths and thermal conductivity were decreased. Tensile strengths at ambient temperatures ranged from 50 to 2500 psi and flexural strengths from 50 to 5000 psi. These strengths were found to increase with density, but the increases were not proportional to the percentage increase of theoretical density.

The investigators suggested that foamed molybdenum may have application where low weight, vibration damping, and low thermal conductivity are required while retaining the basic physical properties of the metal.

TRW has reported that Mo-0.5Ti alloy has been chosen for study in Phase II of its process development program for precision radial-forging integral-turbine wheels.(12) The objectives of this program are to optimize the processing techniques for forming selected superalloys and refractory alloys into high-strength, close-tolerance turbine wheels, and to demonstrate reproducibility of properties and dimensional control. The program is divided into three phases as follows:

- Phase I - Process improvement and qualification of materials
- Phase II - Process refinement
- Phase III - Process verification and integrity of product.

Mo-0.5Ti alloy was selected over TZM and Cb-752 alloys for study in Phase II because it was found to be more amenable to forging into the required blade configurations and met the desired high-temperature strength requirements.

TZM alloy is being evaluated as the structural material for the wheel and blades in the potassium-vapor turbine of the SNAP-50/SPUR power plant. Because the turbine wheel is to be fabricated from a forging, AiResearch Manufacturing Company of Arizona, together with the cooperation of various commercial vendors and fabricators of TZM, is studying the influence of forging parameters and carbon contents on the mechanical properties of TZM forgings. A TZM pancake forging, 9-1/2 inches in diameter and 1-3/4 inches thick in the stress-relieved condition, was tested by Battelle(13) for Charpy unnotched-specimen transition temperature and short-time tensile properties at 1400 to 2000 F. The forging was found to be nonhomogeneous with respect to transition temperature. The most ductile part became brittle below about 200 F, while the most brittle part changed from ductile to brittle behavior at about 275 F. The tensile strength was influenced to some degree by the vertical location of the tensile specimen in the forging. The specimens adjacent to the top surface of the forging were stronger than specimens taken from the center location. The creep behavior of this material is being evaluated and will be covered in a separate report.

Long-time, high-vacuum creep data for molybdenum TZC alloy have been reported by TRW under a NASA contract for potential application in space electric-power-system components.(8) Test data are presented in Figure 3. The data in Figure 3 show that creep does not occur in a uniform manner in TZC alloy, but exhibits periods of rapid extension followed by an absence of creep or even contraction of the specimen. The occurrence of the specimen contraction coupled with limited post-test examination indicated that strain-induced precipitation produced the low creep rate in the TZC material. Tests will be continued to determine the long-time creep behavior of molybdenum-base alloys.

TUNGSTEN

Most commercially available ionizers have a surface pore density of 10^5 pores/cm^2, but, in an

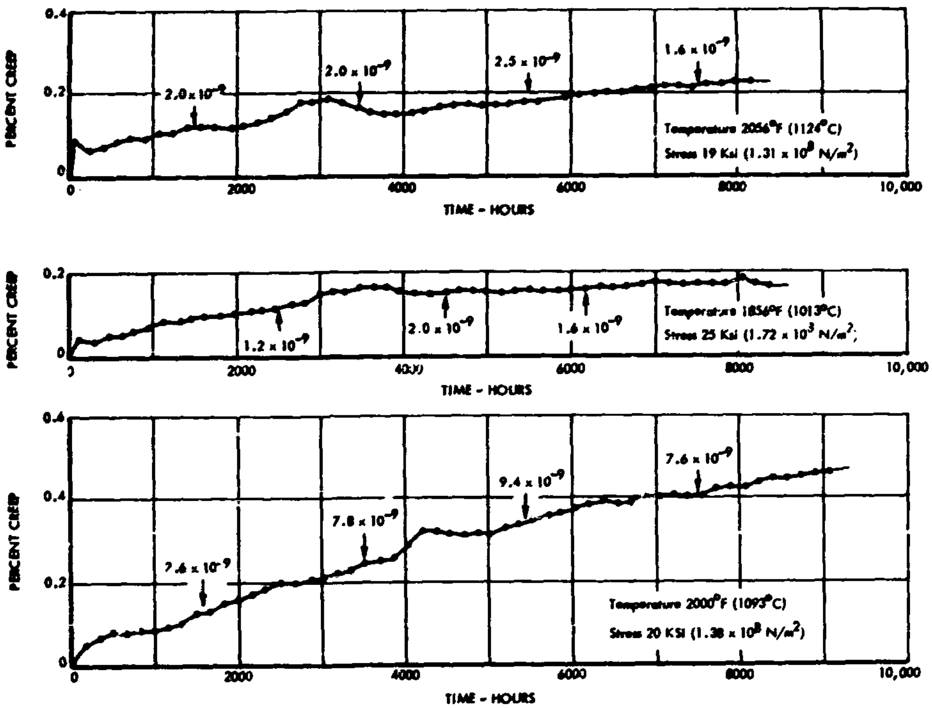

FIGURE 3. CREEP DATA FOR ANNEALED (1 HOUR AT 3092 F) MOLYBDENUM TZC ALLOY AT 1856, 7000, AND 2056 F[8]

investigation at TRW to determine the characteristics and behavior of porous structures formed from spherical tungsten powders, an increase to 10^6 pores/cm^2 was achieved.[14] Improvement was effected in part by semi-isostatic pressing of sized powders which were doubly enclosed by specially selected elastomeric materials. For one particular powder lot of 3.6-micron average particle diameter, the following parameters were obtained: 6.6×10^6 pores/cm^2 average surface pore density, 1.9-micron average pore diameter, and a specific permeability of 4.6×10^{-11} cm^2. It appears on the basis of this work that further gains in ionizer characteristics will be realized through the use of more closely classified starting powders.

In further research at Electro-Optical Systems, a high-performance, low-density ionizer of considerable promise has reached an early development stage.[15] Ionizers were prepared from fine angular tungsten powder with additions of copper flake to increase the pore-to-solid ratio and boron nitride to minimize structural changes in service. The ionizers were characterized by low densities (less than 70 percent), coarse pore structures, excellent thermal stability at 1600 to 1800 C (2912 to 3272 F), and economy of fabrication. Data to date indicate that ionizers capable of over 10,000 hours of effective operation at 1100 to 1200 C (2012 to 2192 F) have been developed. The contractual design goal of 10,000 hours' operation at 1100 to 1400 C (2012 to 2552 F), with density, permeability, and pore-size changes of less than 1 percent, is still to be achieved.

In related work on a NASA contract, pore densities up to 8×10^6 pores/cm^2, depending on original particle size of fine spherical tungsten powder, have been obtained at Hughes Research Laboratories.[16] The highest pore densities were obtained with 2.4-micron powder and the lowest (1×10^6 pores/cm^2) with 6.9-micron powder.

The Bureau of Mines has developed a procedure in which low-density tungsten powder billets are extruded into rods and sheet bar by high-energy-rate forming equipment.[17] Starting with billets sintered to approximately 60 percent of theoretical density (2 hours at 1100 C), extrusion was carried out at reduction ratios of 6.25 to 1 at 1230 C (2246 F) and 9 to 1 at 1800 C (3272 F). Resultant yield strengths were higher than those ordinarily obtained by conventional powder-metallurgy techniques, but ductility was lower. It is believed that preheating billets in hydrogen prior to HER extrusion would improve ductility.

The use of a plasma torch to build up pore-free tungsten deposits is described in a foreign publication.[18] The tungsten solidifies on a tungsten substrate with a cast microstructure. The use of the torch as a localized heating source for tungsten forging, the build up of tungsten-ceramic composites, and the production of spherical tungsten powder is also noted.

Ram speed has been found to be a critical factor in the extrusion of billets to produce tungsten tubing at Oak Ridge.[19,20] Whereas a ram speed of 2 in./sec is sufficient for extruding aluminum, brass, or steel, ram speeds of at least 5 and preferably 8 in./sec are required to extrude tungsten and particularly tungsten-base alloys. At lower ram speeds, loss of heat from the billet increases the yield strength to beyond the press capacity. As part of the same tubing program, fabrication by the

thermochemical deposition (TCD) of WF_6 and/or ReF_6 with hydrogen is under study. Tungsten sheet has also been rolled from TCD specimens. Table 3 presents experimental creep data for TCD tungsten loaded in a direction normal to columnar grain boundaries. Although some scatter is evident, the data approximate those obtained for powder-metallurgy tungsten. At 2200 C (3992 F), TCD tungsten shows a trend of increasing fracture ductility with increasing rupture time. This trend is associated with grain-boundary movement in directions more nearly parallel to the loading direction. Figure 4 compares the creep-rupture properties of the TCD material with those of other tungsten materials used in this investigation.

Stress-rupture measurements on 5-mil Type 218CS (doped, cleaned, straightened) wire indicate higher strength than that for other forms of tungsten (alloys excluded) in the 1200 to 2500 F temperature range.[21] It is suggested as a leading fiber candidate for composite reinforcement. Although tungsten has an unfavorably high density as compared with superalloys, the doped wire investigated remained stronger by a factor of five when stress for 100-hour rupture life to density ratio values were compared.

A study of tungsten additives in terms of their grain-refining capabilities pointed toward boron as the most effective.[22] A nominal addition of 0.5 wt.% decreased the average columnar-grain diameter in electron-beam melted metal from 0.48 to 0.008 centimeter. The effectiveness of the elemental additions decreased in the following order: boron, yttrium, carbon, hafnium, zirconium, molybdenum, columbium, rhenium, and tantalum. The losses of these elements during melting also decreased in approximately the same order. Elemental additions were generally more effective grain refiners than refractory compounds. Elements with the smallest distribution coefficients were the most effective grain refiners.

Singleton has studied the tungsten-oxygen interaction.[23] At all pressures studied and at temperatures below 1500 K, the temperature dependence of the rate for oxygen reacting with tungsten was approximately linear, consistent with the model of a single rate-determining step having a constant energy of activation (33 kcal/mole). At temperatures above 1500 K, the rate of oxygen removal was found to pass through a maximum. The transition temperature shifts from 1600 K at 4 x 10^{-8} torr to about 1800 F at 4 x 10^{-5} torr.

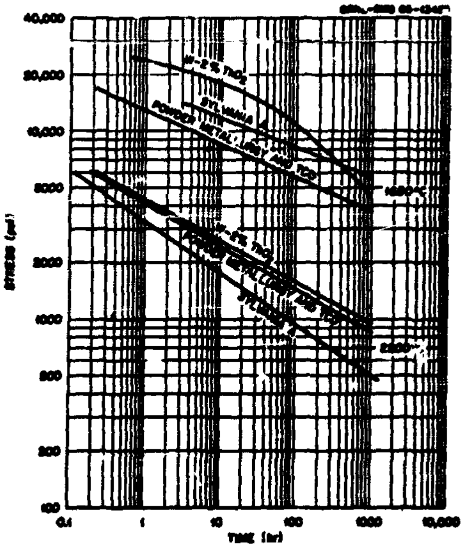

FIGURE 4. COMPARATIVE CREEP-RUPTURE PROPERTIES OF SEVERAL TUNGSTEN-BASE ALLOYS INCLUDING THERMOCHEMICALLY DEPOSITED (TCD) TUNGSTEN[20]

TABLE 3. CREEP-RUPTURE PROPERTIES OF TUNGSTEN SHEET FABRICATED BY THERMOCHEMICAL DEPOSITION[20]

Surface Treatment	Stress, psi	Time to Indicated Strain, hour					Rupture Strain, percent	Minimum Creep Rate, %/hr
		1%	2%	5%	10%	Rupture		
				Tested at 1650 C (3000 F)				
Lapped	6000	7.4	19.2	--	--	30.5	4.2	0.063
Lapped	4000	5.0	35	185	390	593.7	21.0	0.020
None	6000	7.3	--	--	--	9.7	6.3	0.083
None	6000	4.7	11.0	--	--	12.8	3.1	0.12
None	5000	35	102	--	--	176.5	3.5	0.016
Lapped	4000	20	225	--	--	413.0	3.2	0.0040
				Tested at 2200 C (3990 F)				
Lapped	1346	1.0	2.7	6.5	13.0	62.9	35.0	0.75
Lapped	2000	0.5	1.4	4.6	10.3	21.3	21.9	1.1
None	1500	4.7	9.3	18.0	29.3	35.7	16.6	0.19
Lapped	1250	4.0	48	160	306	789.9	29.2	0.026
None	2000	0.7	2.0	--	--	4.3	4.2	0.77
Lapped	2000	0.4	0.6	1.0	1.6	1.85	15.6	2.8
Lapped	2000	1.0	1.5	2.4	3.7	5.05	21.8	1.0
None(a)	2000	1.2	2.1	3.15	4.4	5.3	21.9	0.85
Lapped	2000	0.5	1.4	2.3	3.1	4.65	21.6	1.33

(a) Annealed 90 hour at 1650 C (3000 F) prior to loading.

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